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Post-combustion carbon dioxide capture: Evolution towards utilization of nanomaterials

Zhi Hua Lee, Keat Teong Lee, Subhash Bhatia, Abdul Rahman Mohamed *

Low Carbon Economy (LCE) Research Group, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

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ABSTRACT

Carbon dioxide (CO_2) is not the gas that gives the most severe global warming impact among the greenhouse gases (GHGs). However, its highest annual emission into the atmosphere makes it the most imperative anthropogenic GHG. This elevated emission is primarily coming from fossil fuel power plants. Hence, post-combustion CO_2 removal from power plants becomes crucial in global warming mitigation as it can be retrofitted directly into an existing plant. CO_2 removal technology nowadays is utilizing solvent-based sorbents, such as amine solutions and ionic liquids. Many extensive research works have been carrying out to improve the constraints of existing technology. In this paper, a general review on existing CO_2 removal technologies, existing research works on CO_2 removal sorbents was done. In conjunction with that, we will look into the potential and development of nanomaterials as CO_2 removal sorbents in the future. Nanomaterials have shown their potentials in CO_2 capture with its high surface area and adjustable properties and characteristics. Many limitations in existing technology were found improvable by nanomaterials.

Contents

* Corresponding author. Tel.: +60 4 599 6410; fax: +60 4 594 1013.
E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

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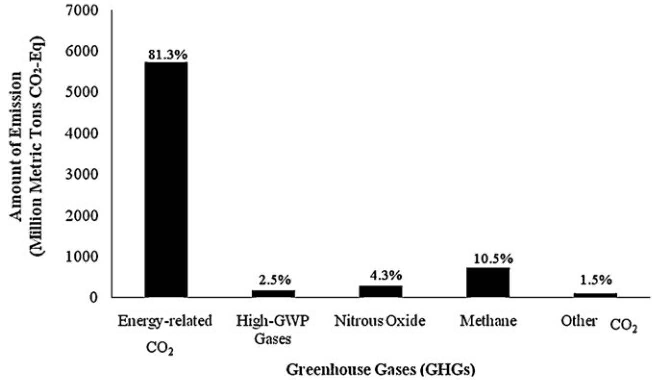


Fig. 1. GHGs emissions in United States by year 2008 [3]. High-GWP gases referred to high global warming potential gases, e.g. hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6).

1. Introduction

Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6) have been listed in Kyoto Protocol 1998 as greenhouse gases (GHGs) [1]. CO_2 are the most important GHG because it emission is notably high compare to the others. CO_2 emission was recorded at 29.6 billion metric tons by year 2007 compared to 21.9 billion metric tons by year 1997 [2] and yet the figure is increasing from time to time. In United States, one of the highest CO_2 emission country, CO_2 emission is 81.3% of the total GHGs emitted [3]. By 2007, global CO_2 concentration hit 383 ppm which was 37% higher than pre-industrial period level [4]. Other GHGs concentrations are relatively low. For instance, concentration of CH_4 and N_2O in the atmosphere were only 1774 part per billion (ppb) and 319 ppb, respectively, during 2005 [5]. Fig. 1 shows the comparison of the anthropogenic GHG emission in United States by year 2008. The data is reported in unit CO_2-equivalent (CO_2-eq), which is used to compare emission of different GHGs by counting their accumulated radiative forcing towards global warming effects over a given time period. Apparently, CO_2 gave highest impact to global warming among all the listed GHGs.

In nature, CO_2 will be absorbed by earth, either by weathering of rocks, photosynthesis of plants or ocean sinks by photosynthesis of marine plankton [6]. These natural sinks phenomena have balanced the natural source of CO_2 emission into the atmosphere over centuries. Excessive emission of CO_2 since industrial era has made these natural removals became not sufficient anymore to maintain the CO_2 concentration in the atmosphere. CO_2 which was not being absorbed accumulated in the atmosphere and result in a drastic raise in CO_2 concentration. Every 3–5 gigatonnes of carbon will contribute to 1 ppm raise of CO_2 concentration in the atmosphere [7]. During the 1970s, CO_2 concentration in atmosphere increased by 1.3 ppm per year and this figure became 2.2 ppm per year by 2007 [4]. Fig. 2 shows the increasing trend of global CO_2 emissions and its concentrations over years. Intergovernmental Panel of Climate Change (IPCC) predicted 2–3 °C of temperature increase from now [8] is dangerous, while Hansen et al. [9] argued that 1 °C rise of global temperature is the maximum tolerance for global warming to prevent the melt of the ice sheet and precious species extinction. To prevent global warming from endangering the world, climate models estimated that CO_2 concentration cannot exceed 450 ppm [9]. Scientist predicted the safe value for CO_2 concentration in atmosphere is 350 ppm while CO_2 concentration of the atmosphere is 383 ppm nowadays [4]. Hence, ideally, no more daily emission of CO_2 is allowed yet the live-long GHG in the atmosphere need to be removed.

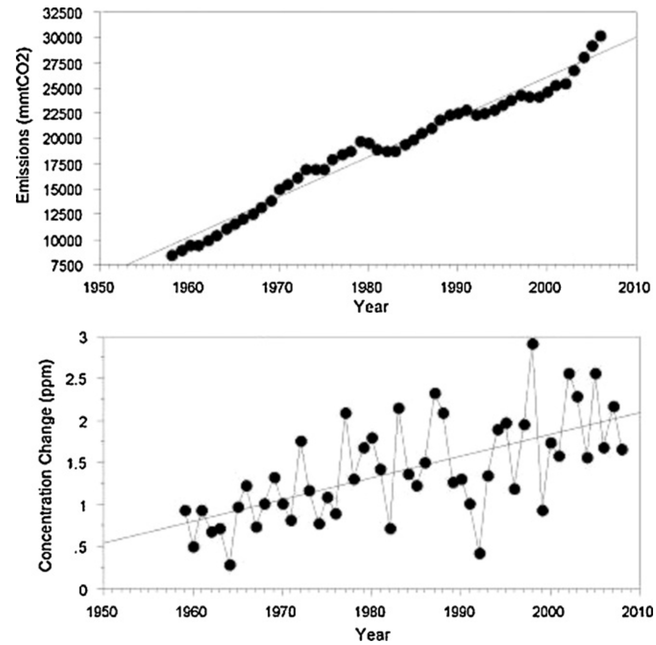


Fig. 2. (Top) Annual total global CO_2 emission; (bottom) annual change in CO_2 concentration [84].

1.1. Main CO_2 sources

Energy supply sector contributed apparently higher emission (26%) compared to the other sectors in GHGs emission as shown in Fig. 3a. This sector is particularly referred to fossil fuel (including coal, natural gas and oil) power plants which are dominant in generating and supplying electricity (Fig. 3b). As second major CO_2

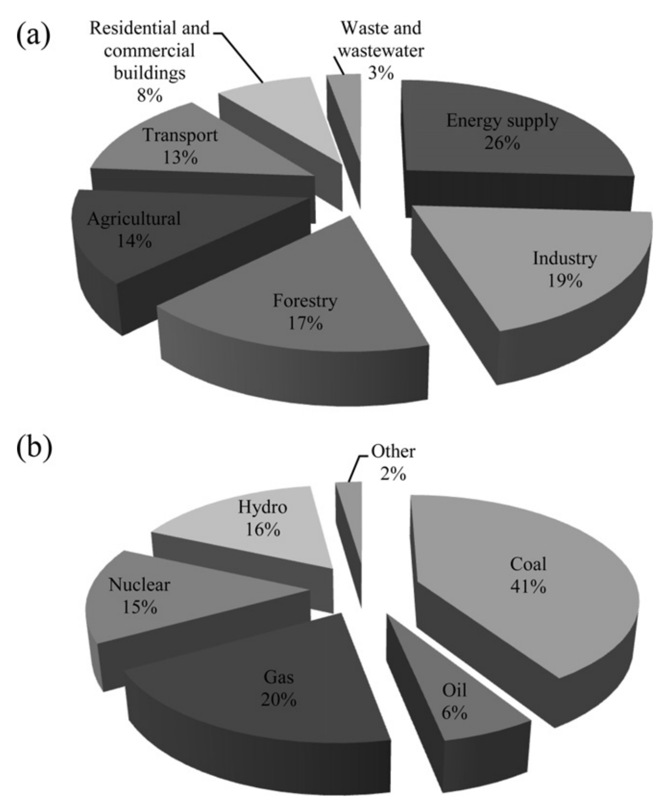


Fig. 3. (a) Total anthropogenic GHG emissions from different sectors in 2004 (in terms of CO_2-eq) [5]. (b) Total world electricity generation in 2006 [22].

contributor, CO_2 emission from industry sector is mainly come from chemicals, petrochemicals, iron and steel, cement, paper and pulp, and other minerals and metals production [10]. In the meantime, CO_2 is also emitted from forestry sector, attributed by degradation of leftover plant materials and soil carbon after deforestation [11]. Usage of fossil fuel in agricultural industries [12], as well as transportation is the main source of the CO_2 emission. There is small portion of CO_2 emissions come from residential sector or applications, waste and wastewater.

In order to reduce energy-related CO_2 emissions, new-designed power plants and renewable energies have been developed to reduce or eliminate these GHGs emission. However, they are still at a very preliminary stage to replace traditional fossil fuel power plants. In the near future, fossil fuel plants are quite impossible to be totally substituted. Fossil fuel, includes coal, natural gas and petroleum, will still remain as the most important source of energy in this century due to its wide availability and economical viability [13]. Our review is focussed on CO_2 removal from fossil fuel power plants.

Generally, fossil fuel power plants can be classified into pulverized coal (PC) power plants, integrated gasification combined-cycle (IGCC) power plants, and natural gas combined-cycle (NGCC) power plants. The most common and conventional type of power plants is PC power plants. PC power plants contribute to the global electricity generation of 1000 GW, meanwhile IGCC power plants recorded only 7 GW of electricity generation [14]. The brief process of PC power plants (without CO_2 capture) is illustrated in Fig. 4. CO_2 concentration emitted from PC power plants is about 14% by volume [15]. This value is different depends on the power plant type. Other components of flue gas are oxygen (O_2), nitrogen (N_2), water vapour, and trace amount of sulphur dioxide (SO_2) and nitrogen oxide (NO).

1.2. Carbon capture and storage (CCS)

In order to reduce CO_2 emission into the atmosphere effectively, carbon capture and storage (CCS) strategy has been introduced. CCS can be defined as a wide range of technologies that are implied to remove and store CO_2 in a safe manner before it is emitted into the atmosphere. It is associating with many components of technologies, including capturing, transporting and storing of CO_2 [16]. It can be additionally added to the existing plants. This system requires less additional energy compared to the other CO_2 removal concepts and has an applausive result in the reduction of CO_2 emission. This strategy is effective to remove CO_2 from large emission sources like fossil fuel plants, industrial processes such as cements and iron plant, and fuel processing plant such as oil refineries and natural gas processing [17]. However, an unavoidable penalty on the energy and cost of the operating plant, are the main challenges of CCS [18]. Consequently, CCS will only be applied when plant operators see the benefits for removing CO_2 from their plants or execution of legislation on this environmental issue is done [19]. In order to encourage the employment of CCS, techno-economic aspect is of paramount importance, where CCS needs new effective technologies with low operation costs [20].

2. Existing CO_2 removal technologies and researches

CO_2 capture and storage technology in fossil fuel power plants nowadays can be categorized into three basic routes, namely [18]:

(a) Pre-combustion capture,
(b) Oxy-fuel combustion capture, and
(c) Post-combustion capture

Schematic diagram of these CO_2 capture routes in fossil fuel plant is illustrated in Fig. 5. Just as implied by its name, pre-combustion capture is a process where CO_2 is captured and stored before the gas produced from fossil fuel is passed through the combustion process. In another words, this method is applying the concept of decarbonizing fuel before it is used in electricity production [17]. Oxy-fuel combustion uses high purity oxygen, about 95%, to combust with fuel, instead of ambient air. Flue gas produced from this process consists of mainly CO_2 and condensable water, where CO_2 is more easily separated out from the gas stream [21].

In post-combustion capture, CO_2 is removed from the flue gas after the combustion. This is the most feasible approach as it can be retrofitted into the existing process without much modification of the existing plants. The processes mainly involve chemical absorption, physical adsorption, membrane and cryogenic separation. Chemical absorption and physical adsorption gain more focus because cryogenic separation requires high energy, while most membrane separation methods are still at their development stage [22].

2.1. Existing technologies on CO_2 removal

Recently, the most applied technology in CO_2 removal in power plant is the post-combustion capture with solvent stripping/sorption. Table 1 shows the operational details of three main licensed processes. Kansai Electric Power and Mitsubishi Heavy Industries Ltd. employ their patented sterically hindered amine solution, which requires lower regeneration energy, in their process [23]. Table 2 shows some of the CO_2 capture projects in power plants which apply this technology.

Alkaline amine-based solution is the major choice as solvent with its affinity towards acidic gas, CO_2. The reaction occurred is explained by zwitterion mechanism which is generally accepted and discussed elsewhere [24,25]. There are two major units in this process, namely absorber and stripper. Absorber is the place where CO_2 absorption process takes place. Exhausted solvent is then channelled to stripper where the regeneration step is done. Process illustration of CO_2 capture by alkaline amine-based solution is shown in Fig. 6.

However, post-combustion CO_2 capture technology is facing some constraints when it is applied for large flue gas flow from fossil fuel power plants anyway. It causes a drop in the power plant efficiency by approximately 10% and the CO_2 removal cost is US$30–50 per ton CO_2 [26]. The process also requires a high thermal energy, about 4 GJ per ton CO_2 in regeneration process for most common amine-based solution, 30 wt% monoethanolamine (MEA) [27]. In the mean time, flue gas pre-treatment is needed for a solvent absorption/stripping process. Gas SO_2 and NO removal is essential prior to CO_2 removal. These acid gases will form heat stable salt with the alkaline solution absorbent where the reaction is irreversible and undesirable [28]. Besides that, concentration of amine solution used in the process is limited due to its viscosity and foaming properties [29]. Corrosion is another problem faced in the process [30].

2.2. Existing researches works on CO_2 removal

Recent researches in CO_2 removal are focused on discovery of new liquid sorbents, development of novel dry-based sorbents, and modification of the existing sorbents.

2.2.1. New liquid sorbents

Ammonia (NH_3), which is the basic structure of amine group, was predicted to have lower energy consumption than monoethanolamine (MEA). Modelling work showed that 5 wt%

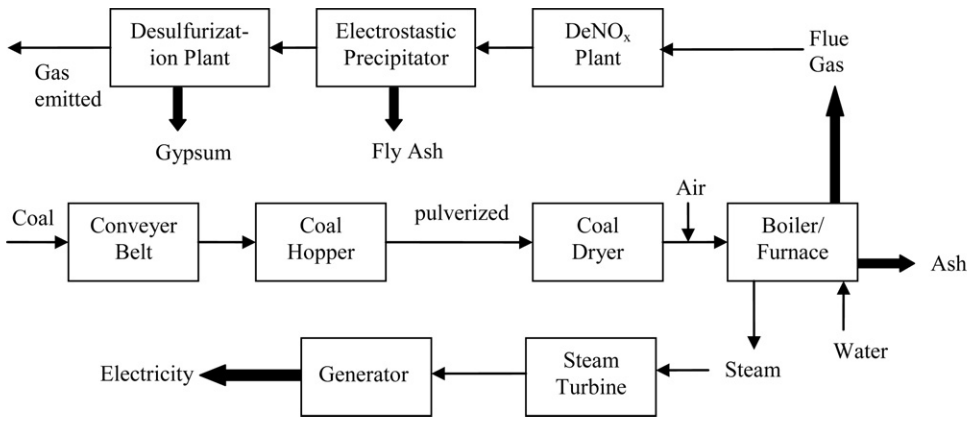


Fig. 4. Schematic process diagram of pulverized coal (PC) power plant [14,85].

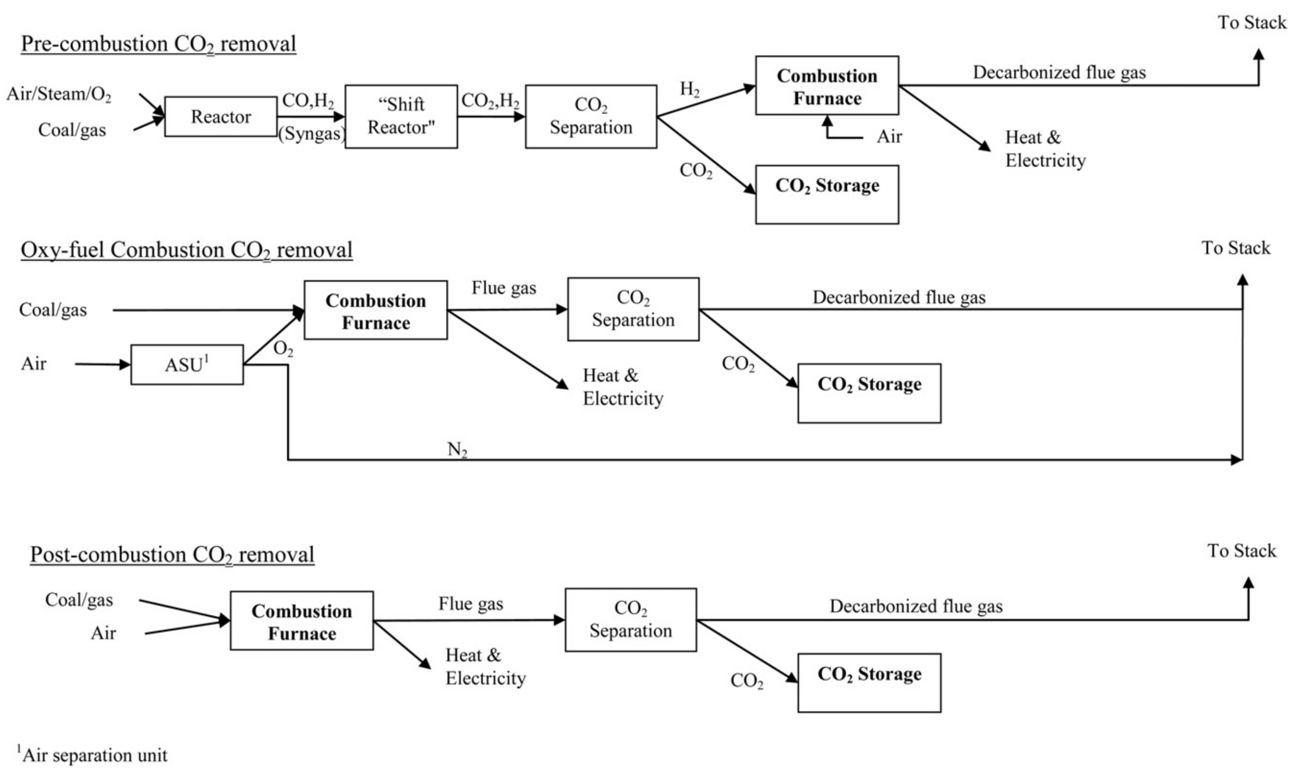


Fig. 5. Schematic diagram of different CO_2 capture routes.

Table 1
Three commercially available CO_2 capture processes by solvent absorption with their key performance parameters [86].

	Kerr–McGee/ABB Lummus crest process	ECONAMINE^{TM}	Mitsubishi KS-1
Licenser	ABB Lummus	Fluor Daniel	Kansai Electric Power and Mitsubishi Heavy Industries. Ltd.
Steam for solvent regeneration	2.3–3.0 t/t CO_2	1.94 t/t CO_2	1.5 t/t CO_2
Solvent flow rate	25 m^3/t CO_2 (estimated)	17 m^3/t CO_2	11 m^3/t CO_2
Electricity for fans and pumps	100–300 kWh/t CO_2	110 kWh/t CO_2 (GTCC[a]) 40 kWh/t CO_2 (PCF[b])	11 kWh/t CO_2 (PCF[b])
Cooling water	75–150 m^3/t CO_2	165 m^3/t CO_2	150 m^3/t CO_2 (estimated)
Solvent consumption	0.45 kg/t CO_2	1.5–2.0 kg/t CO_2	0.35 kg/t CO_2
Activated carbon consumption	Not available	0.075 kg/t CO_2	Not available
SO_2-tolerance	<100 ppm	<10 ppm	<10 ppm

[a] Gas turbine combined-cycle.
[b] Pulverized-coal-fired plant.

Table 2
Carbon capture and storage (CCS) projects by using post-combustion process [87].

Project	Location	Plant capacity (MW)	Technology	Capacity (MT CO_2/year)	CO_2 use	Start-up year
AEP Mountaineer	West Virginia, USA	1300 (Phase1) 235 (Phase 2)	Post[1]-Chilled NH_3 absorption	0.1 (Phase 1) 1.5 (Phase 2)	Sequestration	2009 (Phase 1) 2016 (Phase 2)
WA Parish	Texas, USA	60	Post[1]–Fluor Coporation Econamine FG Plus	0.5	EOR[2]	2013
Trailblazer	Texas, USA	600	Post[1] – Flour Corporation Econamine FG plus	5.75	EOR[2]	2014
Kemper City	Mississippi, USA	582	Post[1]–IGCC + TRIG technology	N/A	Sequestration	2014
HECA	California, USA	390	Post[1] – IGCC (for petroleum coke)	2.0	EOR[2]	2014
Antelope Valley	North Dakota, USA	120	Post[1]-NH_3 absorption	1.0	EOR[2]	2012
Project Pioneer	Alberta, Canada	450	Post[1]-Chilled NH_3 absorption	1.0	Sequestration and EOR[2]	2015
Bow City	Alberta, Canada	1000	Post[1]-Amine scrubbing	N/A	EOR[2]	2014
Belchatow	Poland	250–858	Post[1] – Alstom's advanced amines capture technology	1.8	Sequestration	2011–2015
Ferrybridge	West Yorkshire, UK	500	Post[1] – with supercritical pulverized coal retrofit	1.7	Sequestration	2011–2012
Longannet	Fife, Scotland, UK	330	Post[1] – Aker Clean Coal's technology	N/A	Sequestration	2014
Kingsnorth	Kent, England, UK	2 × 800	Post[1]	1.9	Sequestration	2014
Maasvlkte	Rotterdam, Netherlands	1100	Post[1]	5.0	Enhanced gas recovery	2015
Porto Tolle	Porto tolle, Italy	660	Post[1] – capture with amine-based solution	1.5	Saline formation	2015
FINNCAP	Meri Pori, Finland	565	Post[1] – IGCC	1.25	Sequestration	2015
Kårstø	Rogaland, Western Norway	420	Post[1]–capture with amine-based solution	1.2	Sequestration or EOR[2]	2011–2012
Husnes	Hordaland, Norway	400	Post[1]	2.6	EOR[2]	2011
Mongstad	Mongstad, Norway	350	Post[1]	2.5	Sequestration in saline formation	Waiting for funding

NH_3 usage in CO_2 absorption has similar energy consumption with 30 wt% MEA at low operating temperature (10 °C) [26]. The constraints for NH_3 to become an ideal solvent absorbent are precipitation of ammonium salt in the absorption unit and volatility of the solvent. Recently, chilled NH_3 has been utilized as solvent absorbent in many CO_2 capture and storage projects [31]. Other amine-based solutions have been extensively studied to improve the CO_2 absorption capacity of MEA absorption process. Methyldiethanolamine (MDEA) is a secondary amine-based solvent which is widely studied for its CO_2 absorption activity. It has a better selectivity towards CO_2, higher CO_2 absorption capacity, more thermal stability, lower alkalinity, lower volatility, lower corrosion and energy consumption [32,33]. However, it has a slower absorption rate [33]. Activator, piperazine (PZ) was added into this amine-based solution and found to have better performance in CO_2 absorption [32,34]. The activated MDEA also has explored

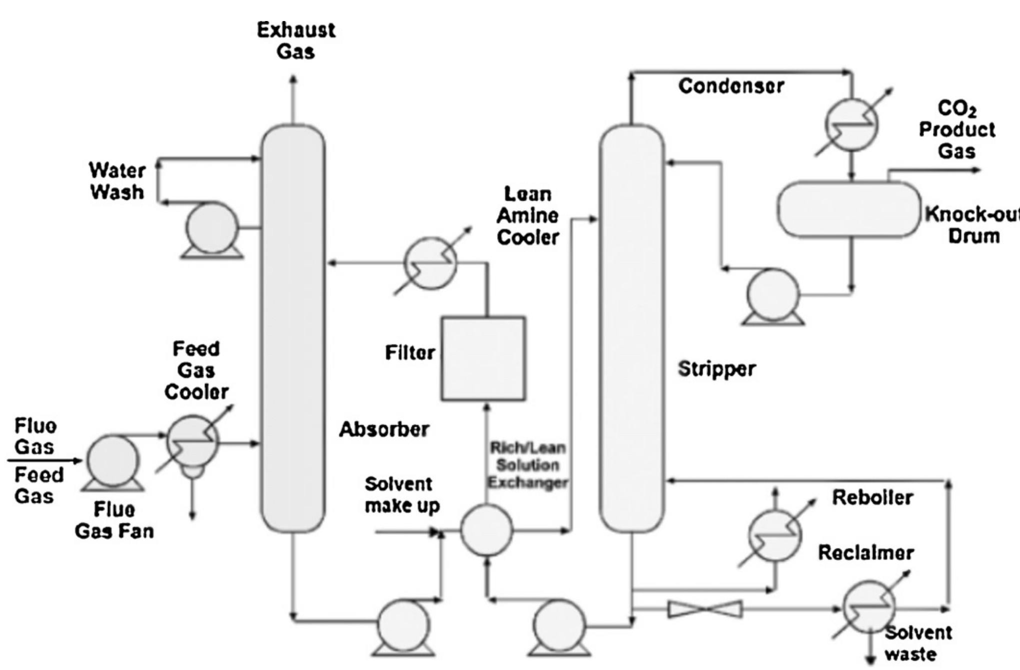


Fig. 6. Typical process diagram of CO_2 capture using solvent absorption in industry [28].

an improvement towards thermal and oxidative degradation [35]. Many other activators or blenders have been used to improve the performance of the amine-based liquid sorbent. MDEA was given a boost in CO_2 absorption capacity when it was blended with triethylene tetramine (TETA) [36]. MEA was blended with 2-amino-2-methyl-1-propanol (AMP) and the solution showed an improvement in CO_2 capture capacity and absorption rate compared to the individual solution [24].

Ionic liquid is another solvent sorbent which is well-established in research and has been started in industry by ION Engineering, a Colorado based company [37]. This is an organic salt that in a stable liquid form below 100 °C [33] with a combination of inorganic or organic anion and large organic, bulky asymmetric cation [38]. Its properties can be adjusted by choosing different combination of anion and cation pair. Wide liquid range, thermal stability, negligible vapour pressure, tuneable physio-chemical characteristic and high CO_2 solubility are some of the properties of ionic liquid which favours its utilization in CO_2 removal applications [39]. High viscosity is the major drawback of this liquid solvent. Bates et al. [40] designed 'task-specified' ionic liquid (TSIL), which used imidazolium cation specifically for CO_2 capture. TSIL had a comparable CO_2 molar uptake rate with MEA and the reaction was reversible. Galán Sánchez et al. [38] functionalized ionic liquid with amine group and successfully enhanced the performance of the ionic liquids in CO_2 capture. In order to overcome the constraints in both amine-based solution and ionic liquids, these two solvents have been blended together. For instance, amino acid-based ionic liquids had been mixed with MDEA [33]. CO_2 absorption capacity of this combination was double of mixture MDEA and MEA. Table 3 summarized some of the researches with their advantages over existing sorbents.

2.2.2. Dry-based sorbents

Development of a dry-based sorbent in CO_2 post-combustion capture is always a desire when liquid sorbents used in industries nowadays are still facing many constraints, such as corrosion, foaming, low removal rate with large-size equipments needed etc. Dry-based sorbents are normally easier for handling and causing fewer issues during the operation. Research works in this sorbent type is classified into inorganic and organic sorbent.

Inorganic sorbent are mostly metal compounds. A wide range of metals salts have been studied, from alkali metal compounds (i.e. lithium silicate, lithium zirconate) [41–44] to alkaline earth metal compounds (i.e. magnesium oxide and calcium oxide) [45–47]. Theoretically, one mole of metal compound can react with one mole of CO_2 with a reversible reaction as shown in reactions (1)–(3).

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3 \quad \text{(Lithiumsilicate)} \tag{1}$$

$$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2 \quad \text{(Lithiumzirconate)} \tag{2}$$

$$XO + CO_2 \leftrightarrow XCO_3 \quad (X = \text{alkalineearthmetal}) \tag{3}$$

Hence, dry-based solvent will have comparably higher CO_2 capture capacity to the liquid sorbents in terms of mol CO_2/kg sorbent. Table 4 shows comparison of CO_2 absorption capacities among these sorbents with organic sorbents. Considerable attentions were paid to calcium oxide (CaO) as it has a high CO_2 absorption capacity, and high raw material availability (e.g. limestone) at a low cost. Lithium salts recorded a good performance in CO_2 absorption, too, but it gained less focus due to its high production cost [48].

Organic sorbents are mostly referred to the carbonaceous and siliceous materials. Carbon atoms (for carbonaceous material) or silicate ions (for siliceous material), SiO_4^-, form continuous network among themselves [49], to become a giant and porous structure with high surface area. Activated carbon is the common example of carbonaceous materials while siliceous materials are represented by zeolites, MCM-41, MCM-48, SBA-15, SBA-12, SBA-16 etc. Different surface functional groups found on activated carbon, including carboxyl, carbonyl, phenol, quinone, lactone, have made it an efficient adsorbent [50]. Researchers have tried to modify and tailor the structures of these materials to generate a novel adsorbent which is techno-economically suited to CO_2 capture. Fabrication of molecular sieves [51], pore-expanded siliceous materials [52,53] and utilization of waste materials as siliceous or carbonaceous sources [54–56] are some of the common approaches done.

2.2.3. Sorbents' modification

CO_2 capture capacities of activated carbon and siliceous materials were not satisfying and lower than amine-based solutions and metal compounds. Many attempts [52–54,57] have been done to add amine-based functional group on these porous materials. The purpose of those approaches was to mimic a dry-based amine-based absorbent. Amine-based solution was loaded by impregnation method onto the porous surfaces [58,59]. By utilizing the high porosity and surface area of these dry-based sorbent, CO_2 capture capacities of the modified sorbent has been successfully increased. The main constraints of the modified sorbents are limited CO_2 capture capacity (limited amine functional groups), limited operating temperature range, and volatility of the amine-solution. A comparison can be made between some modified sorbents in Table 5.

3. Nanomaterials as sorbents in CO_2 capture

Nanomaterials are materials with at least one dimension equals to or less than 100 nm [60]. When the materials are synthesized in nanoscale regime, many size-dependent specific properties will be shown up; including adsorptive property [61]. Unique properties like light weight, and small size with high surface area have put nanomaterials as an alternative choice for gas adsorption applications [62]. In this review, we divided these nanomaterials into three categories, namely nanoporous materials, nano-hollow structured materials and nanocrystalline particles.

3.1. Nanoporous materials

Nanoporous materials are classified as porous materials with pore diameters between 1 and 100 nm [63]. These materials show relatively high surface area compare to non-porous materials. Their pore size and structure can be tailored, make them as desirable choice in adsorption [64]. Some nanoporous materials have been used for a long period, such as activated carbon and zeolites. Designed and tailor-made nanoporous materials specifically for CO_2 removal are focused in this section.

Xu et al. [58,65] designed selective 'molecular basket' by grafting polyethylenimine (PEI) uniformly on MCM-41. The sorbent was prepared by wet impregnation method, where mixture of MCM-41 and PEI was prepared in methanol medium. Its preparation was followed by drying process. CO_2 molecules were captured by active sites of PEI doped in MCM-41 mesopores in a condensed 'basket' form. In their experiment, the adsorption activity was selectively towards CO_2 and stable throughout the adsorption/desorption cycles. CO_2 adsorption capacity of the sorbent was 24 times higher than MCM-41 and 2 times higher than PEI [65]. Franchi et al. [52] and Serna-Guerrero et al. [53] expanded the pore size of MCM-41 for amine-based functional group grafting. Pore-expended MCM-41 was synthesized by a post-synthesis hydrothermal treatment with a pore-expender agent. The expanded pore size was 11.7 nm compared to 3.3 nm for the original MCM-41 [53]. More amine active sites were grafted with a larger pore size and hence enhanced CO_2 adsorption activity. In addition, the sorbent also had excellent stability and did not deteriorate in the presence of moisture.

Table 3
Some of the research works on discovery of new liquids sorbents with their advantages.

Category	Liquid sorbents	Advantages	Limitations	Ref.
Amine-based solvent	Ammonia	Form stable salt with CO_2 which is potentially used as raw material in fertilizer industry. Energy consumption can be reduced when solvent regeneration process is avoided.	- Precipitation of ammonium salt - Volatility of the solvent	[26,88]
	MEA[a]	High process efficiency High reaction rate with CO_2	-Energy-insentive -Corrosion and high volatility	[89,90]
	MDEA[b]	Lower volatility, thermal stability, less alkaline, higher CO_2 load, less regeneration cost among amines.	-Slow reaction rate	[33]
Amines mixture	Mixture of two amines (MEA[a] + AMP[c])	AMP[c] has better absorption capacity than MEA[b] while MEA[b]'s efficiency is higher. This combination gives a liquid sorbent which is optimum in both.	-Limited absorption capacity	[24]
	MDEA[b]/Piperazine (PZ)	Greater stability than MEA[b] (30–50%). Piperazine prevents thermal degradation of MDEA[a]. Lower heat of absorption (75 kJ/mol) compare to MEA (84 kJ/mol).	-PZ's activity dropped with temperature and CO_2 loading on it.	[35]
Ionic liquids	Functionalized ionic liquids	Improved CO_2 absorption performance compare to ionic liquids. Lower surface tension than aqueous amine solution	-High viscosity than ionic liquids -Long regeneration period -Drop of performance after regeneration	[38]
	'Task specific' ionic liquids	Ionic liquid with specific functional cation designed for CO_2 removal Comparable CO_2 removal rate to MEA solution.	-High viscosity	[40]
Ionic liquids + amine-based solution	Amino acid-based ionic liquids + MDEA[b]	Ionic liquids aid to reinforce CO_2 absorption on MDEA[a] solution. Selective, absorption activity towards N_2 is very small. High regeneration efficiency (>98%)	-Unknown sorbent stability and performance in for abundant cycles	[33]

[a] Monoethanolamine.
[b] Methyldiethanolamine.
[c] 2-Amino-2-methyl-1-propanol.

Table 4
Some of the dry-based sorbents with their CO_2 capture capacities.

Dry-based sorbent	Operating temperature (°C)	Operating pressure (kPa)	CO_2 capture capacity (mol CO_2/kg sorbent)	Ref.
Lithium zirconate	400	100	5.0	[91]
Lithium orthosilicate	600	100	6.13	[91]
Calcium oxide	600	100	17.3	[91]
Magnesium hydroxide	200	1034	3.0	[92]
Magnesium oxide (mesoporous)	100	100	2.27	[66]
Activated carbon	30	110	1.58	[93]
MCM-41	25	100	0.62	[53]

Metal oxides have been also produced in nanoporous form. Bhagiyalakshmi et al. [66] produced mesoporous MgO for CO_2 adsorption. MgO precursor solution penetrated into a porous carbon exotemplate. The solution was dried in vacuum whilst mesoporous MgO was formed. Template was burnt off in a calcination process afterwards. The sorbent was a regenerable, selective and thermally stable sorbent. The mesoporous material enabled higher diffusion rate of CO_2 molecules and thus increased the CO_2

Table 5
Comparison of CO_2 capture capacities of pure and amine-enriched activated carbon and siliceous materials.

Sorbent	Operating temperature (°C)	Operating pressure (kPa)	CO_2 capture capacity (mol CO_2/kg sorbent)	Ref.
Activated carbon (AC)	30	30	0.35	[94]
AC(4%KOH)	30	30	0.55	[94]
AC(EDA[a] + EtOH[b])	30	30	0.53	[94]
AC(4%KOH + EDA[a] + EtOH[b])	30	30	0.64	[94]
MCM-41	25	100	0.62	[53]
MCM-41(DEA[c])	75	100	1.26	[52]
MCM-41 (50% PEI[d])	75	100	2.52	[57]
MCM-41 (50% PEI[d]) "molecular basket"	75	100	2.95	[58]
PE[e]-MCM-41	25	100	0.50	[53]
PE[e]-MCM-41(TRI[f])	25	100	2.85	[53]
PE-MCM-41(DEA[c])	75	100	2.36	[52]
MCM-48	25	100	0.033	[54]
MCM-48(APTS[g])	25	100	0.639	[54]

[a] Ethylenediamine.
[b] Ethanol.
[c] Diethanolamine.
[d] Polyethyleneimine.
[e] Pore-expanded.
[f] Triamine-contained silane.
[g] 3-Aminopropyltriethoxysilane.

adsorption capacity by MgO. Maximum CO_2 removal of this sorbent was about 10 times higher than commercial non-porous MgO.

3.2. Nano-hollow structured materials

The hollow-structure can be illustrated as a material with a combination of shell and core [67]. Nano-hollow structured materials are hollow-structured materials synthesized in nano regime. This structure gives many added properties to the chemical compounds. Thus, it becomes one of the desired structures when more specific functional materials are in demand [68].

Carbon nanotubes (CNTs) are most famous among nano-hollow structured materials with their dimension ranges from 1 to 10 nm in diameter and 200 to 500 nm in length [69]. They have been applied in CO_2 adsorption. Alexiadis and Kassinos [70] studied the interaction between CO_2 molecules and CNT. The CNT walls were CO_2-philic compounds where CO_2 formed stronger attraction with CNT walls rather than other CO_2 molecules. A highly concentrated CO_2 environment was created in hollow core of CNT. Cinke et al. [71] investigated CO_2 capture by single-walled carbon nanotubes (SWNTs). Physical adsorption was the dominant activity of the process and adsorption capacity decreased with temperature. In addition, purified SWNT adsorbed CO_2 better than unpurified SWNT. Meanwhile, Su et al. [72] investigated multi-walled carbon nanotubes (MWNTs) CO_2 adsorption from flue gas stream. The affinity of MWNT towards CO_2 was improved by amine-group grafting on the nano-hollow structured material. The research has been extended by Hsu et al. [73] in study on the cyclic operation of sorbent CNTs. Desorption was done by thermal regeneration since the CO_2 adsorption process is an exothermic process. Desorption duration was shortened by running the regeneration under a vacuum condition. MWNTs showed stability for 20 cycles of adsorption and regeneration.

Besides CNT, CaO is another material which was developed in nano-hollow structured form. Decay of sorbent throughout multiple absorption and desorption cycles is the major drawback of this absorbents. This is caused by the sintering effect [74], volume increase of reacted absorbents (decrease of distance between absorbents) and high Tamann temperature [75]. Yang et al. [76] developed a novel structure of pod-alike nanosized CaO hollow particles for CO_2 capture and improved the stability of CaO against its decay problem. The $CaCO_3$ nanopods were first prepared through a precipitation process when CO_2 was bubbling through a calcium hydroxide ($Ca(OH)_2$) slurry in the existence of polymer block. CaO nanopods were obtained by calcination of the produced $CaCO_3$ nanopods. Absorption capacity of CaO nanopods (17.5 mol CO_2/kg sorbent) was apparently higher than commercial CaO (12.1 mol CO_2/kg sorbent). Besides, the absorbent was sustainable towards multiple CO_2 absorption/regeneration cycles. It managed to retain more than 50% CO_2 absorption after 50 absorption–desorption cycle compared to 25% in commercial CaO.

3.3. Nanocrystalline particles

Nanocrystalline particles refer to the crystalline particles which are synthesized under nano regime. Synthesis of particles in nanosized will produce a homogenous narrow size distribution of the material. Particles in nano regime promise an enhanced ability to chemically absorb a wide range of molecules, especially organic molecules which comprise of most environmental pollutants [61].

A comparison has been made on CO_2 capturing capacity between sorbent with different particle sizes. The result showed that sorbent with tetragonal phase and smaller particle size have better performance in absorption [77]. Tetragonal nanocrystalline Li_2ZrO_3 prepared by Ochoa-Fernández et al. [78], through a novel soft-chemistry route, with crystalline size of 14 nm, had given a rise in CO_2 capture. This nanocrystalline Li_2ZrO_3 achieved 27 wt% absorption capacity in 5 min compared to the normal Li_2ZrO_3 that need 24 h to achieved 18 wt% absorption capacity. The sorbent was also more stable in CO_2 absorption/desorption process and maintained the capturing capacity after 7 cycles. Khomane et al. [41] also reported the same observation from their research with lithium silicate. By synthesizing lithium silicate nanoparticles through sol–gel method mediated with reverse microemulsion, nanoparticles with size 4–12 nm were obtained. Its maximum CO_2 absorption capacity was reported as 5.77 mol CO_2/kg sorbent at 610 °C, with retention time of 25 min. Essaki et al. [79] investigated flue gas removal using packed-bed lithium silicate pellets. At the temperature of 600 °C, its CO_2 absorption capacity was reported 5.0 mol CO_2/kg sorbent which was relatively low compare to the lithium silicate nanoparticles.

Li et al. [75] improved the stability and sustainability of CaO absorbent by adding inert $MgAl_2O_4$ spinel nanoparticles, which were small rod-like spinel nanoparticles. The absorbent was synthesized through a physical mixing route where the CaO and $MgAl_2O_4$ were mixed in a wet medium followed by calcination step. Nanospinels have increased the surface area as well as pores volume of the absorbent. The addition of inert prevented the agglomeration and enhanced the stability of CaO absorbent. The absorbent was able to maintain its initial absorption capacity after 115 cycles with CO_2 absorption capacity of 35 wt%. Inert did not involve in CO_2 absorption activity. Hence, CO_2 absorption capacity decreased when the CaO composition became less in the absorbents.

CaO derived from nano-sized $CaCO_3$ showed its sustainability throughout 30 absorption/desorption cycles with high absorption of CO_2 [74], which was better compared to previous research. Unique morphology of the sorbent, which was affected by the nanoparticle size distribution, was the main factor that contributed to sorbent's high absorption capacity. However, sorbent decay problem still persisted like other CaO sorbents. Wu et al. [80] reported that nano CaO/Al_2O_3 sorbent had a higher adsorption capacity and decomposition rate than micro CaO/Al_2O_3. This nanomaterial also had a lower regeneration temperature due to its larger surface energy. It was prepared through chemical route where nano calcium carbonate and aluminium sol was mixed with sodium hexametaphosphate. Its maximum capacity was recorded at 6.02 mol CO_2/kg sorbent at 650 °C. It retained 68.3% absorption ratio after 50 adsorption/desorption cycles while micro CaO/Al_2O_3 was retained only 40% absorption ratio after 14 cycles. Table 6 shows the details of CO_2 capture activity of various nanomaterial sorbents with their advantages and disadvantages.

3.4. Nanomaterials as a better sorbents

Nanomaterials have higher surface area than their ordinary materials. Adsorption capacity is proportionally related to the surface area of the adsorbents. Higher surface area provides more sites of reaction and hence boosts the adsorption or absorption capacity. Mesoporous MgO synthesized by Bhagiyalakshmi et al. [66] had high surface area (250 m^2/g) and the adsorption capacity was 75% higher than non-porous MgO. Mesoporous structure enabled physical adsorption activity by metal oxide at low temperature. CaO nanopods produced by Yang et al. [76] had relatively higher surface area (16.92 m^2/g) than commercial CaO (0.40 m^2/g). From their CO_2 absorption study, CaO nanopods absorbed 17.5 mol CO_2/kg sorbent while commercial CaO absorbed only 12.1 mol CO_2/kg sorbent.

Besides having high surface area, many unique properties and characteristics are shown up in nanomaterials. This enables nanomaterials to give an enhancement in their sorption activities. CNTs were reported with surface area of 567 m^2/g for SWNTs [81], and 394 m^2/g for MWCNTs [82]. With the same surface area, CNTs have apparently higher adsorption capacity compared to other

Table 6
List of CO_2 nanomaterial sorbents with their operation details, CO_2 capture capacities and regeneration information.

Sorbents	Operating temperature (°C)	Operating pressure (kPa)	CO_2 concentration (%)	CO_2 capture capacity (mol CO_2/kg sorbent)	Regeneration temperature (°C)	Regeneration duration (min)	Regeneration cycles, n	CO_2 capture capacity remained after n cycles (%)	Ref.
'Molecular basket' MCM-41(50%PEI)	75	100	99.8	2.5	75	150	8	96.0	[65]
PE-MCM-41(TRI)	25	100	100	1.8	75	30	10	94.4	[53]
PE-MCM-41(DEA)	25	100	n/a	2.9	75	90	7	96.6	[52]
Mesoporous MgO	25	101	99.9	1.8	800	60	3	100	[66]
MWNT	60	101	15	1.3	–	–	–	–	[73]
MWNT	60	101	50	1.7	–	–	–	–	[73]
CaO nanopods	600	101	60	17.5	700	n/a	50	61.1	[76]
CaO derived from nanosized $CaCO_3$	650	101	15	16.7	850	10	100	22.2	[74]
CaO–$MgAl_2O_4$ (Spinel Nanoparticles)	650	101	30	9.1	850	30	65	84.6	[75]
Nano CaO/Al_2O_3	650	101	33.3	6.0	800	5	15	61.7	[80]
Lithium silicate nanoparticles	610	101	n/a	5.77	–	–	–	–	[41]
Nanocrystalline Li_2ZrO_3 particles	575	101	100	6.1	650	n/a	8	100	[78]

high-surface-area materials, namely activated carbon and siliceous materials. Lu et al. [82] compared the adsorption capacity of MWCNTs with granular activated carbon (GAC) and zeolite. GAC and zeolite had higher surface area (954 m^2/g and 788 m^2/g, respectively) compared to MWCNTs (394 m^2/g). Under a same adsorption condition tested, MWCNTs recorded CO_2 adsorption capacity as 1.57 mol CO_2/kg sorbent while activated carbon and zeolites, which had double surface area double than MWCNTs adsorbed only 1.65 mol CO_2/kg sorbent and 1.44 mol CO_2/kg sorbent, respectively. Cinke et al. [71] studied the same subject with HiPCO purified SWNT and activated carbon. They observed that HiPCO purified SWNTs which had only 25% higher surface area than activated carbon recorded one-fold higher CO_2 adsorption capacity. Table 7 shows the comparison of the CO_2 adsorption capacity between CNTs, activated carbon and zeolites. It is worth noticed that CNTs have larger pore size as compared to other carbonaceous materials. Larger pore sizes enable more surface areas become approachable by the adsorbates (CO_2). In addition, uniform structure of the tailor-made CNTs also eases the diffusion of adsorbates to the physical adsorption sites. CaO found its way to prevent the sorbent decay problem during the absorption process when it was in nano-structure [75,76,80]. This is because many size-dependent characteristics will be shown up when a material is synthesized in nano regime.

Nanomaterials also offer advantage as their structure can be tailor-made to improve the properties and characteristics of a compound or element. For instance, CNTs are able to be produced in different dimensions and diameters. This reflected that nanomaterials are potential to be tailor-made up to their desired properties. Pore-expanded MCM-41 is another example. Expanding the pores of MCM-41 has prevented the pore-clogging of it after grafted with amine-based functional group [52,53].

4. Techno-economic view of nanomaterials as CO_2 removal sorbents

Besides having good CO_2 capture ability, cost and profit of the process is an important issue of concern. The cost of a complete CO_2 removal process includes sorbents, process installation and commissioning, operating and maintenance, additional fuel

Table 7
Comparison of the CO_2 adsorption capacity between CNTs, activated carbon and zeolites.

Sorbents	Surface area (m^2/g)	Total pore volume (cm^3/g)	Temperature (°C)	Pressure (kPa)	CO_2 adsorption capacity (mol/kg sorbent)	Additional information	Ref.
Raw SWNT[a]	567	n/a[c]	35	107	2.00	CO_2 was dosed incrementally onto the sample tubes at different pressures.	[71]
HiPCO purified SWNT[a]	1617	1.55			5.36		
Activated carbon	1284	n/a[c]			2.23		
MWCNT[b]	394	0.91	25	100	1.57	Gas stream: 50% CO_2 Gas flow rate:0.08 L/min Sorbent quantity: 1.0 g	[82]
Granular activated carbon	954	0.48			1.66		
Zeolites	788	0.35			1.44		
MWCNT[b]	407	0.45	20	100	0.64	Gas stream: 15% CO_2 Gas flow rate:0.08 L/min Sorbent quantity: 1.0 g	[72]

[a] Single-walled carbon nanotubes.
[b] Multiwalled carbon nanotubes.
[c] Not available.

resources; and CO_2 compression, transport and storage [48,83]. Efficiency decreases of power plant will cause a loss to the plant operator, too.

To develop a sustainable CO_2 removal system, many factors have to be considered when a novel sorbent is synthesis. Sustainability of the sorbent will be the prior factor to be looked into. While having a high CO_2 capture capacity, a sorbent must be sustainable throughout multiple sorption/desorption cycles. Decay or loss of sorbent will need a high sorbent make up flow, which is costly. The sorbent should have a low production cost. Thus, it is preferable to have a low-cost, widely available raw material and a simple synthesis process. For instance, lithium salts has been reported to be a good sorbent in CO_2 removal. However, its high raw materials' price makes it gain fewer attentions than other metal salts. According to Abanades et al. [48], cost of lithium carbonate (Li_2CO_3) is $4.47 per kg whereas $CaCO_3$ (CaO's raw material) cost is only $0.005 per kg. CNT with specific structure is only available at extremely high price (US$ 5/g) compared to GAC which cost of US$ 1/kg [72].

A CO_2 removal system that operates at around flue gas emission temperature will be ideal. In this case, no extra energy is needed to heat up or cool down the emitted flue gas. Additional energy used for the system will eventually reduce the power plant's efficiency. Reproducibility of the CO_2 captured will be an added advantage for the system. When CO_2 can be reproduced from the system for industry usage, the system will become a profitable process. Sorbents' selectivity is another crucial factor to be focussed. In a system that aims to recovery CO_2 for industry usage, a sorbent with high CO_2 selectivity is preferable.

5. Future prospect of the research in nanomaterial sorbents

Nanomaterials are potential sorbents to overcome many limitations of CO_2 capture process. They have relatively high CO_2 capture capacities, sustainable throughout multiple sorption/desorption cycles, and some of them have relatively low energy requirement. The main drawback of these nanomaterials is complicated, precise and costly synthesis process. In order to tailor and control their sizes and dimensions, synthesis of nanomaterials commonly needs specific materials which are costly, and the method used is complicated. Besides than screening and identifying an ideal nanomaterial sorbent, future research works should focus on designing simple and low-cost production route of these nanomaterials. This will be followed by a scale-up and process study for the sorbent. In addition, development of a CO_2 selective sorbent is preferable where pure CO_2 can be extracted from the sorbent as another carbon source for industry. This will make CO_2 removal process economically feasible.

6. Conclusion

High stability of CO_2 in the atmosphere has made its removal become very challenging. Various sorbents have been developed and improved, but still there exist many limitations with the sorbents handling and operation process are still exists. An ideal sorbent for CO_2 removal is yet to be discovered. Nanomaterials have shown their potentials in CO_2 capture with their high surface area and adjustable properties and characteristics. Many structural limitations have been improved by nano-structured materials. However, nanomaterials are always related to high production cost with complicated synthesis process. This will be most important scope that needs to be focussed in future research works.

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